

Heterogeneous Chemistry important in the Polar Stratosphere

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Abstract

Aircraft emissions have been thought to enhance the formation of polar stratospheric clouds (PSCs) in the Arctic winter, and therefore heterogeneous reactions on the surfaces of these clouds may accelerate the polar ozone depletion. In this paper laboratory studies of heterogeneous processes, such as the uptake of HCl and heterogeneous reactions of ClONO_2 and HOCl with HCl, on both Type I and Type II PSCs will be presented.

The uptake of HCl in water ice and nitric acid ice films has been investigated in a flow reactor interfaced with a differentially pumped quadrupole mass spectrometer. These studies were performed under experimental conditions that may mimic the polar stratosphere. The HCl uptake in ice films at 188 K and 193 K was determined to be in the range of 8.7×10^{13} to 1.8×10^{15} molecules/cm² (if the geometric area of the flow reactor, 290 cm², was used in the calculation) when HCl partial pressures of 7×10^{-8} to 6×10^{-6} Torr were used. Based on a model which accounts for the total surface area of the films, the true surface density could be a factor of 25 lower than that calculated by the geometric area. A slightly higher uptake was observed at the lower temperature of 188 K. The uptake of HCl in ice was significantly enhanced by using an HCl partial pressure greater than 1×10^{-5} Torr. The observation was found to be consistent with the formation of hexahydrate or trihydrate of HCl according to the phase diagram of the HCl/H₂O system.

The uptake of HCl in nitric acid ice at 188 K was determined to be in the range of 8.0×10^{13} to 5.3×10^{14} molecules/cm² at a HCl partial pressure 4.5×10^{-7} Torr. Measurement of both HNO₃ and H₂O vapor pressures was made to positively identify the formation of nitric acid trihydrate (NAT) surface according to the phase diagram of the HNO₃/H₂O system. The HCl uptake in NAT is comparable to that in water ice in the present experiment, but significantly smaller than the previously reported values.

Heterogeneous reactions of HOCl + HCl → Cl₂ + H₂O (1) and ClONO₂ + HCl → Cl₂ + HNO₃ (2) on ice surfaces at a temperature of 188 K have also been investigated in a flow reactor interfaced with a differentially pumped quadrupole mass spectrometer. Partial pressures for HOCl and ClONO₂ in the range of 6.5×10^{-8} Torr to 2.0×10^{-6} Torr, which mimic conditions in the polar stratosphere, have been used. Uptake of HCl on ice surfaces using partial pressures of HCl in the range of 1.8×10^{-7} Torr to 8.0×10^{-6} Torr has been measured prior to contact with HOCl or ClONO₂. Pseudo-first-order decays of HOCl and ClONO₂ over HCl-coated ice surfaces have been observed in all experiments under the conditions of $P_{\text{HOCl}} < P_{\text{HCl}}$ and $P_{\text{ClONO}_2} < P_{\text{HCl}}$ used. Both the decay rates of HOCl and ClONO₂ and the growth rates of Cl₂ have been used to obtain reaction probabilities: $\gamma_g(1) = 0.34 \pm 0.20$ (1σ) and $\gamma_g(2) = 0.27 \pm 0.19$ (1σ) if we assume that the area of ice surfaces is equal to the geometric area of the flow-tube reactor. The results are in good agreement with previous measurements. By considering the morphology of ice films, we obtain true reaction probabilities $\gamma_t(1) = 0.13 \pm 0.08$ and $\gamma_t(2) = 0.10 \pm 0.08$ using a previously published model of surface reaction and pore diffusion. In addition, the true reaction probability, $\gamma_t(3)$, for the ClONO₂ + H₂O → HOCl + HNO₃ (3) reaction has been measured to be greater than 0.03 on ice surfaces. Reaction mechanisms for these heterogeneous reactions (1) - (3) are discussed, including a possible two-step mechanism for reaction (2) in terms of reaction (3) and reaction (1).